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Fabrication of magnesium germanide nanorods from Ge nanorod templates

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Abstract

Mg germanide nanorods were successfully fabricated by interdiffusion of the Mg into Ge nanorods on Si substrates at 425 °C for 0.5 h. It was observed that the Mg₂Ge nanorod structures were formed by an interdiffusion process between the deposited Mg atoms and the Ge nanorods. Moreover, Mg₂Si nanorods were formed by additional interdiffusion between the Mg₂Ge nanorods and the Si substrates at 425 °C for 4 h. The structural properties of the Mg₂Ge and Mg₂Si nanorods were characterized, and the growth evolution of the structural and morphological properties of the nanorods was discussed.

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Keywords: magnesium germanide; nanorod; interdiffusion; growth evolution

1. Introduction

Recently, semiconducting silicide nano-structures have attracted much attention based on their unique properties and complex structure as new energy conversion materials [1]. β -FeSi₂ nanodots were directly formed on Si substrates [2], and the nanowires were formed using Si nanowire templates [3]. In addition, it

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was reported that the thermoelectric property of nano-scaled materials was expected to be improved, compared for that of the bulk materials [4]. $\text{Mg}_2\text{Si}_{1-x}\text{Ge}_x$ is reported as one of the promising thermoelectric materials in the middle temperature range [5]. However, it is difficult to fabricate the Mg_2Si or $\text{Mg}_2\text{Si}_{1-x}\text{Ge}_x$ nano-structures using bottom-up or top-down techniques. Recently, it was reported that $\text{Mg}_2\text{Si}_{1-x}\text{Ge}_x$ was easily grown using a $\text{Si}_{1-x}\text{Ge}_x$ template [6]. Hara *et al.* also reported the successful growth of Ge nanorods on Si substrates [7].

In this study, the fabrication of Mg germanide nanorods by the interdiffusion of Mg into the Ge nanorods/Si substrates was investigated. The structural properties of the nanorods were characterized, and the growth evolution of the structural and morphological properties of the nanorods was discussed.

2. Experiment

The Ge nanorods/Si substrates grown by high-temperature glancing angle deposition [7, 8] were used as templates and treated in a Mg vapor. The Mg source and Ge nanorods/Si were placed in a loosely sealed glass container, which was loaded into a vacuum chamber. A schematic illustration of the heat treatment equipment used here is shown elsewhere [6]. Both the substrate and the Mg source in the container were then heated at 400~500 °C for 0.5~4 h. The resultant structures were characterized by an X-ray diffraction technique (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) along with a compositional analysis by energy dispersion spectroscopy (EDS).

3. Results and discussion

Figures 1 show Ge-rods on Si substrates before the heat treatment and resultant nanostructures after the heat treatment under different conditions. It was found that the length of the nanorods became shorter after heating in a Mg vapor at 425 °C versus time from Figs. 1(a) to (d). It shows that the nanorods have no reaction with the Mg vapor at 400 °C by comparing Figs. 1(c) and (e). Furthermore, it shows that the temperature has a significant effect on the diffusion of Mg atoms on the Ge nanorods/Si substrates. The length of nanorods became much shorter above 450 °C as shown in Figs. 1(c), (f) and (g). By comparing the samples treated at 450 °C for 1 h with and without the Mg vapor as shown in Figs. 1(f) and (h), it was found that the shortening of the nanorods could probably be due to the enhanced diffusion of the Ge in the Mg vapor environment.

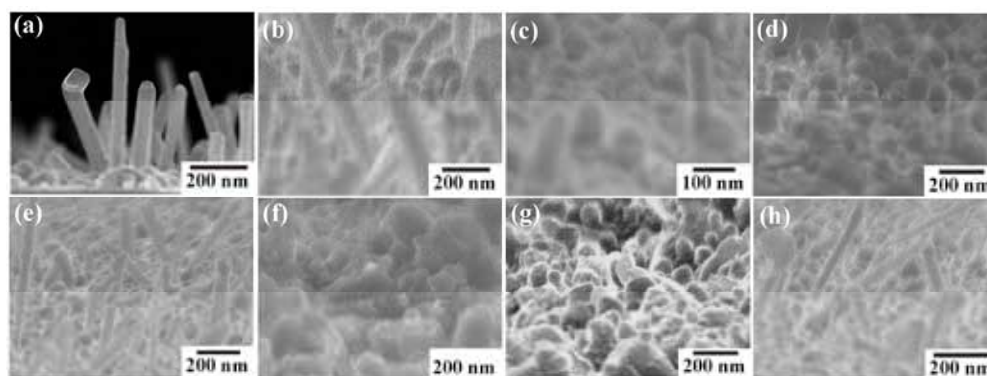


Fig. 1. SEM images of Ge-rods on Si substrates (a) before the heat treatment, resultant nanostructures after heat treatment at (b) 425 °C 0.5 h, (c) 425 °C 1 h, (d) 425 °C 4 h, (e) 400 °C 1 h, (f) 450 °C 1 h, (g) 500 °C 1 h under Mg vapor, and (h) 450 °C 1 h, without Mg vapor.

Figure 2 shows TEM images and the corresponding EDS mappings of the resultant nanostructures after the heat treatment at 425 °C for (a) 0.5 h and (b) 4 h in the Mg vapor. It shows that the nanorod is about ~60 nm in diameter and Mg is homogeneously distributed corresponding to Ge after heating at 425 °C for 0.5 h as shown in Fig. 2(a). The result indicates that the exposure of the Ge nanorods to the Mg vapor leads to the successful formation of the Mg₂Ge nanorod structure. Fig. 2(b) shows that the nanorod becomes thicker, about ~250 nm in diameter, at 425 °C for 4 h. The corresponding mappings show that the nanorod mainly consists of Mg and Si, which suggests Mg₂Si nanorods are formed by additional interdiffusion between the Mg₂Ge nanorods and the Si substrates. It also indicates that Ge atoms in the Mg₂Ge nanorods have diffused into the Si substrates with Mg atoms during the interdiffusion process. It is important to control the treatment time in order to obtain the Mg germanide nanorods.

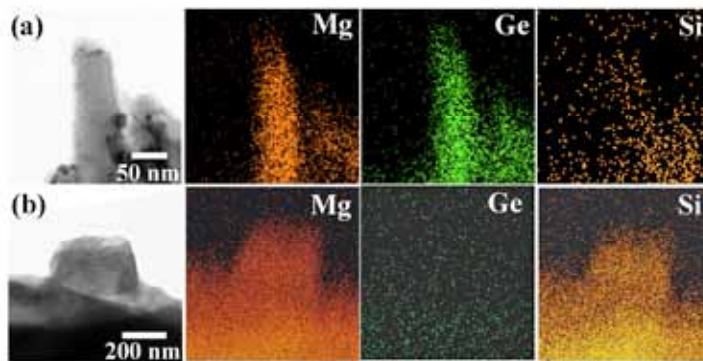


Fig. 2. TEM images and the corresponding EDS mappings of resultant nanostructures after heat treatment at 425 °C for (a) 0.5 h and (b) 4 h under Mg vapor.

Figure 3 shows the HRTEM image and corresponding FFT image of the resultant nanostructure after the heat treatment at 425 °C for 0.5 h as shown in Fig. 2(a). The lattice spacing shown in the figure is 0.21 nm, and the angle is 90 °, which well agreed with those of (202) and (20 $\bar{2}$) of Mg₂Ge of 0.226 nm, which is consistent with the mapping result shown in Fig. 2(a). In addition, it indicates that the growth direction of the Mg₂Ge is [101] as shown in Fig. 3(a).

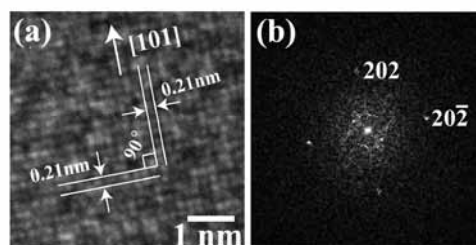


Fig. 3. (a) The HRTEM image and (b) corresponding FFT image of resultant nanostructure after heat treatment at 425 °C for 0.5 h under Mg vapor as shown in Fig. 2(a).

The compound formation mentioned above is interdiffusion-controlled. The interdiffusion coefficient is about 10^{-14} cm²/s for Ge diffusing into Si, and about 10^{-15} cm²/s for Si diffusing into Ge, assuming that Ge has diffused over ~300 nm inside the Si substrate, compared to ~100 nm for Si into Ge as shown in

Figs. 1(a) and (d) at 425 °C. On the other hand, the interdiffusion processes between Ge and Si have been investigated to be about 10^{-17} cm²/s in Si_{1-x}Ge_x around 750–800 °C [9], 10^{-17} cm²/s for amorphous Si/Ge multilayers [10], and 10^{-21} cm²/s in Si_{1-x}Ge_x/Si superlattices at 600 °C [11]. As mentioned above, the interdiffusion between Si and Ge is slower than that observed here. It is considered that the interdiffusion between Ge and Si could be enhanced in the Mg vapor environment. The interdiffusion coefficient between Mg and Si_{1-x}Ge_x has also been reported to be about $\sim 10^{-10}$ cm²/s at 500 °C [6], and estimated as $\sim 10^{-12}$ cm²/s at 800 °C [12]. Especially, the Ge diffusion would be further enhanced than Si due to the Mg diffusion into the Si substrates. A dominant vacancy mechanism has been proposed to explain the Ge–Si interdiffusion phenomenon [9]. It is important that the mechanism of enhanced interdiffusion should be further discussed in detail, which affects the nano-scaled morphology of the structures.

4. Conclusions

The Mg₂Ge nanorods were fabricated by heat treatment of the Ge nanorods on Si substrates in a Mg vapor. It was found that the nanorod size and phases significantly depended on the treatment temperature and time. The Mg₂Ge nanorods were successfully formed by an interdiffusion process between the deposited Mg atoms and the Ge nanorods at 425 °C for 0.5 h, with a diameter size about ~60 nm and growth in the [101] direction. Moreover, the Mg₂Si nanorods were formed by additional interdiffusion between the Mg₂Ge nanorods and the Si substrates at 425 °C for 4h, with a diameter about ~250 nm. The interdiffusion coefficient is about 10^{-14} cm²/s for Ge diffusion into Si, and about 10^{-15} cm²/s for Si into Ge at 425 °C. It was considered that the interdiffusion between Ge and Si could be enhanced in a Mg vapor environment.

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